Lanthanide-Mediated Ligand Transfer Reactions— A Route to Late Transition Metal Bisamido Complexes

Rhett Kempe,* Henrik Noss, and Hans Fuhrmann[a]

Abstract: The reaction of [{O(SiMe$_2$Ap)$_2$}$_2$LnLi(thf)$_n$] **1** (Ln = Nd, n = 2) and **2** (Ln = La, n = 3) in hexane with [(dme)NiCl$_2$] (dme = dimethoxyethane) and [(cod)PtCl$_2$] (cod = 1,5-cyclooctadiene) leads to the dimeric Ni complex [{O(SiMe$_2$Ap)$_2$}$_2$Ni$_2$] (**3**) and the mononuclear platinum compound [O(SiMe$_2$Ap)$_2$Pt] (**4**), respectively (O(SiMe$_2$ApH)$_2$ = bis(4-methyl-2-pyridylamino)tetramethyldisiloxane). Compounds **3** and **4** have been characterized by X-ray crystal structure analysis. The ligand-transfer reactions probably proceed via heterobimetallic intermediates. A model complex of such an intermediate [{O(SiMe$_2$Ap)$_2$}$_2$NdPdMe] (**7**) was isolated by reacting **1** with [(cod)PdMeCl]. Applications of complex **3** in ethylene oligomerization were investigated. Highly branched oligomers with a very narrow molecular weight distribution (M_n = 230 g mol^{-1} (relative to polystyrene standards), M_w/M_n = 1.14) are produced when Et$_3$Al$_2$Cl$_3$ is employed as a co-catalyst and CH$_2$Cl$_2$ as the solvent (TOF = 122 000 h^{-1}). Treatment of one equivalent of **1** or **2** with two equivalents of [(cod)CuCl] results in the formation of the polycyclic tetranuclear complex [{O(SiMe$_2$Ap)$_2$}$_2$Cu$_4$] (**8**). An X-ray crystal structure analysis of **8** shows channels formed by a series of fourteen-membered rings in the solid state.

Keywords: copper · Group 10 elements · lanthanides · N ligands · oligomerization

Introduction

The basics of amido metal chemistry were created at the end of the 1960s and in the early 1970s. Research at this time was mainly focused on exploring the nature of the amido metal bond in comparison to the metal–carbon bond. The rather disappointing findings, however, showed the amido metal bond to be thermodynamically more stable and kinetically rather inert and thus not as interesting as the metal–carbon bond in terms of reactivity studies.[1] Until the middle of the 1980s, only a small amount of interest had been shown in amido–metal chemistry. Cyclopentadienyl ligands and metallocenes as well as stoichiometric and catalytic reactivity of such transition metal complexes had been investigated intensively. Subsequently, Cp-analogous amido ligands were searched for that were somehow related to the well-known cylopentadienyl moiety. Today, the presumed disadvantage of a stable amido metal bond is utilized in amido–metal chemistry to produce well-defined reaction centers in transition metal complexes. In this way, the reactivity of the resulting early transition metal compounds can be specifically tailored to allow applications in areas such as the activation of small, poorly reactive molecules, homogeneous catalysis, or organic synthesis. Insight into the mechanisms of elementary reactions such as C–H activation, α-H elimination, the cleavage of the N≡N triple bond, reactions of N$_2$ with H$_2$ within the coordination sphere of transition metals, new routes for the synthesis of macrocycles, polar metal–metal bonds, and complexes with unusual terminal ligands such as phosphorus, arsenic, or carbon are, in addition to interesting transfer or polymerization reactions, just a few selected examples that illustrate what has become possible by the use of amido ligands. It may be apt to consider this as the renaissance of amido–metal chemistry.[2] What about late metal amido complexes and their reactivity?[3] This chemistry still remains unexplored, probably due to the mismatch of the "hard" amido ligand with the "soft" late metals.[4] Amido metal complexes of Group 10[5] and 11[6, 7] are known but rarely described. Compounds of such metals with bisamido ligands are unknown to the best of our knowledge. The reactivity of late transition metal amido complexes, especially with regard to catalytic applications, promises to be an interesting field, because the weak amido–metal bond may allow efficient generation of catalytically active species.[8]

We report here on the synthesis and structure of Group 10 and 11 bisamido ligand complexes. Applications of one of the compounds in olefin oligomerization are discussed. Bis(aminopyridinato) ligands, which were developed by us, are

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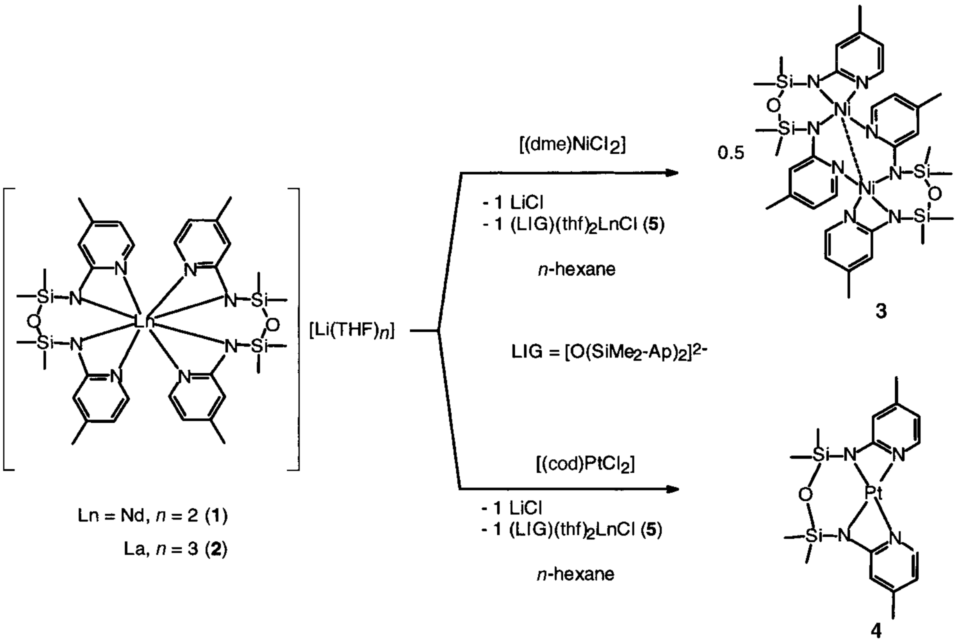
important with regard to the stability of such complexes.[9] Also essential for the transition metal complex syntheses is the concept of the lanthanide-mediated ligand transfer reactions on which we recently communicated.[10]



Scheme 1. Synthesis of **3** and **4**.

Results and Discussion

Amido metal complexes, synthesis, and structure: The reaction of the bis(aminopyridinato) lanthanide ate-complexes **1** and **2** in hexane with $[(dme)NiCl_2]$ (dme = dimethoxyethane) and $[(cod)PtCl_2]$ (1,5-cyclooctadiene; Scheme 1) results in the dimeric Ni complex **3** and the mononuclear platinum compound **4**, respectively. As a by-product of both reactions, in addition to LiCl, monochlorolanthanide species $[O(SiMe_2Ap)_2LnCl(thf)_n]$ (Ln = Nd (**5**) and La (**6**); $O(SiMe_2ApH)_2$ = bis(4-methyl-2-pyridylamino)tetramethyldisiloxane) are formed respectively. The synthesis, structure, and reactivity of such monochloro complexes has recently been described.[18b] The reaction of **1** and **2** with $[(cod)PdCl_2]$ results only in the formation of Pd-black, independent of the solvent used.

Table 1. Data of the X-ray crystal structure analyses.

Compound	**3**	**4**	**7**	**8**
crystal system	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1$/c	$P\bar{1}$
a [Å]	9.998(2)	12.568(3)	13.744(3)	8.500(2)
b [Å]	12.106(3)	8.951(2)	12.948(3)	10.912(2)
c [Å]	18.246(3)	18.492(4)	30.208(6)	12.285(3)
α [°]	83.13(2)	—	—	67.430(12)
β [°]	78.90(2)	105.93(3)	91.96(3)	75.560(13)
γ [°]	67.99(2)	—	—	75.250(12)
V [Å^3]	2006.4(7)	2000.4(7)	5373(2)	1002.7(4)
Z	2	2	4	1
crystal size [mm]	0.5 × 0.4 × 0.3	0.4 × 0.3 × 0.2	0.3 × 0.3 × 0.1	0.1 × 0.1 × 0.1
ρ_{calcd} [g cm^{-3}]	1.335	1.792	1.323	1.562
μ [cm^{-1}](Mo$_{K\alpha}$)	1.096	7.145	1.419	2.252
T [K]	293(2)	200(2)	293(2)	293(2)
θ range [°]	1.82–24.55	2.44–24.26	1.35–21.12	2.23–21.05
no. of reflections	6055	5787	10379	2024
unique	6065	3132	5528	2024
obs. ($I > 2\sigma(I)$)	4546	2548	4299	1472
no. of parameters	433	218	509	226
ωR^2 (all data)	0.096	0.140	0.154	0.137
R value ($I > 2\sigma(I)$)	0.037	0.065	0.049	0.069

Abstract in German: *Die Reaktion von* $[\{O(SiMe_2Ap)_2\}_2LnLi(thf)_n]$ ***1*** *(Ln = Nd, n = 2) und* ***2*** *(Ln = La, n = 3) mit* $[(dme)NiCl_2]$ *bzw.* $[(cod)PtCl_2]$ *in Hexan führt zum dimeren Ni-Komplex* $[\{O(SiMe_2Ap)_2\}_2Ni_2]$ ***(3)*** *bzw. zur einkernigen Platinverbindung* $[O(SiMe_2Ap)_2Pt]$ ***(4)***, $[O(SiMe_2ApH)_2$ = *Bis(4-methyl-2-pyridylamino)tetramethyldisiloxan]. Die Kristallstrukturen von* ***3*** *und* ***4*** *wurden bestimmt. Die Ligandentransferreaktion verläuft wahrscheinlich über heterobimetallische Intermediate. Ein Modellkomplex für eine derartige Zwischenstufe* $[\{O(SiMe_2Ap)_2\}_2NdPdMe]$ ***(7)*** *konnte durch die Umsetzung von* ***1*** *mit* $[(cod)PdMeCl]$ *dargestellt werden. Die Verwendung von* ***3*** *in der Oligomerisierung von Ethylen wurde untersucht. Hochverzweigte Oligomere mit einer sehr engen Molekulargewichtsverteilung* ($M_n = 230\,gmol^{-1}$ *(gegen Polystyrol* $M_w/M_n = 1.14$) *wurden unter Verwendung von* $Et_3Al_2Cl_3$ *als Cokatalysator und* CH_2Cl_2 *als Lösungsmittel* ($TOF = 122\,000\,h^{-1}$) *hergestellt. Durch Umsetzung von einem Äquivalent* ***1*** *bzw.* ***2*** *mit zwei Äquivalenten* $[(cod)CuCl]$ *konnte der polycyclische vierkernige Komplex* $[\{O(SiMe_2Ap)_2\}_2Cu_4]$ ***(8)*** *synthetisiert werden. Die Ergebnisse der Röntgenkristallstrukturanalyse von* ***8*** *belegen, dass im Festkörper Kanäle von vierzehngliedrigen Ringen ausgebildet werden.*

Crystals of **3** suitable for an X-ray structure analysis (Table 1) were obtained from hexane. The molecular structure of **3** and some selected structural parameters are shown in Figure 1. The coordination of the two nickel centers of the dinuclear complex may be best described as nearly square planar. The nickel coordination sphere is formed by one aminopyridinato fragment, one amido-N and one pyridine-N atom; the Ap fragments show N-Ni-N binding angles of 70.08(12) and 69.73(12)°. The lengths of the $Ni{-}N_{amido}$ and $Ni{-}N_{pyridine}$ bonds are nearly the same, as known for aminopyridinato fragments, which act as bridges between the two metal centers. These indicate a delocalized binding mode of the Ap ligands, meaning that the anionic function of the ligand is not localized at the amido-N atom. The

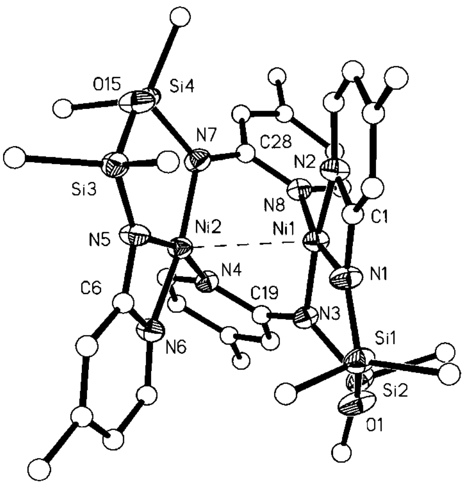


Figure 1. Molecular structure of **3** (ORTEP view; for clarity only atoms regarded significant are drawn as 30% propability ellipsoids). Selected bond lengths [Å] and angles [°]: N1–Ni1 1.910(3), N2–Ni1 1.880(3), N3–Ni1 1.899(3), N4–Ni2 1.890(3), N5–Ni2 1.904(3), N6–Ni2 1.882(3), N7–Ni2 1.920(3), N8–Ni1 1.901(3), Ni1–Ni2 2.7247(15); Si1-O1-Si2 132.5(2), Si4-O15-Si3 133.1(2), N2-Ni1-N8 96.94(12), N3-Ni1-N8 92.80(11), N2-Ni1-N1 70.08(12), N3-Ni1-N1 99.95(12), N6-Ni2-N4 94.50(12), N6-Ni2-N5 69.73(12), N4-Ni2-N7 94.96(12), N5-Ni2-N7 100.40(12).

Ni–Ni distance is 2.7247(15) Å less than twice the van der Waals radius of nickel (1.60 Å).[11] A special characteristic of compound **3** is its dark blue color. Blue to purple colors are normally typical for tetrahedral paramagnetic Ni^{II} high-spin complexes,[12] however, **3** is a diamagnetic compound.

The dinuclear structure of **3** in solution can by verified by NMR spectroscopy. The ^{29}Si NMR spectrum displayed two different resonances, on the other hand, four signals were detected for the methylsilyl group in the ^{1}H NMR spectrum, indicating that the methyl groups are not equivalent, which was confirmed by ^{13}C NMR data.

In contrast to compound **3** the corresponding platinum complex **4** is formed as a light yellow monomer. The NMR spectra show it to be a mononuclear compound in solution due to a single signal set. An X-ray crystal structure analysis of **4** (Table 1) verifies this for the solid state as well. The molecular structure and some binding parameters of **4** are given in Figure 2. The coordination might be best described as square planar. The two Ap moieties, being thoroughly strained, bind to the metal with N-Pt-N angles of 64.4(3)° and 64.6(4)°. It is remarkable how strained Ap fragments can still coordinate late transition metals. The delocalized binding mode for the Ap moieties can be assumed to be the same for **3**. The Pt–N distances are slightly longer (about 0.1 Å) than the Ni–N distances in the Ni complex. This is in accordance with the larger ionic radius of platinum (r(Pt^{2+}) = 0.74 Å vs. r(Ni^{2+}) = 0.63 Å).[13] The radius of the metal center is likely to be the origin for the formation of a mononuclear species.

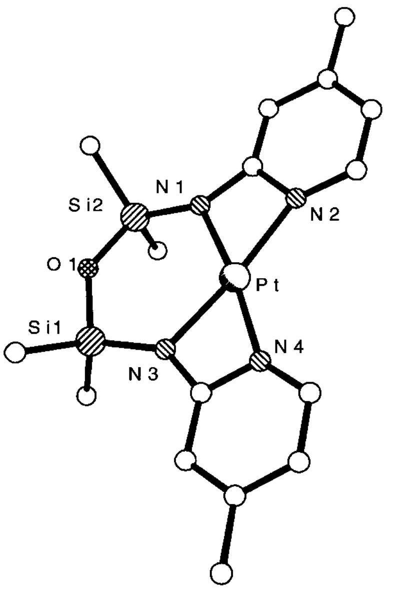
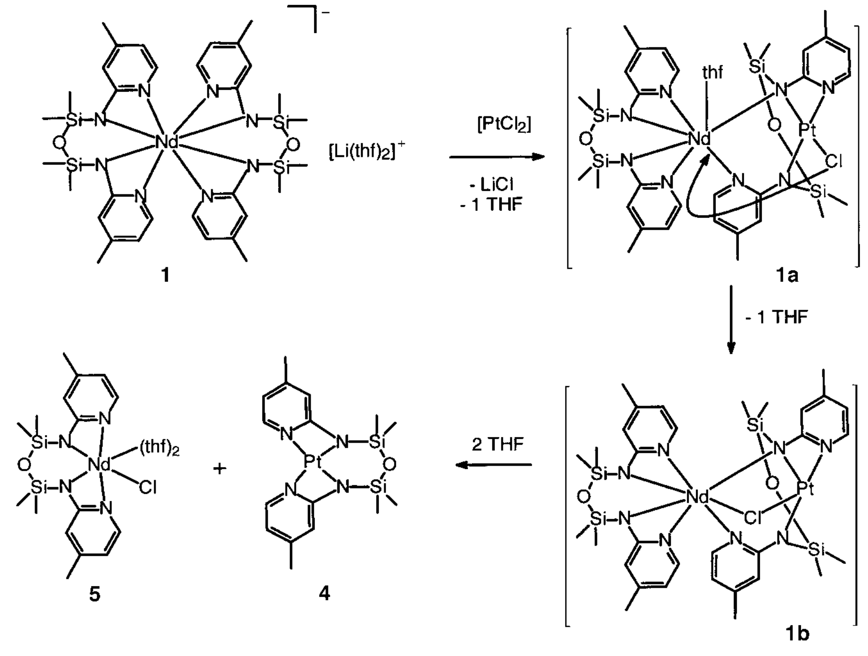


Figure 2. Molecular structure of **4**. Selected bond lengths [Å] and angles [°]: N1–Pt1 2.010(9), N2–Pt1 2.045(9), N3–Pt1 2.022(9), N4–Pt1 2.029(9); Si1-O1-Si2 140.3(4), N1-Pt1-N2 64.4(3), N1-Pt1-N3 108.4(4), N2-Pt1-N4 122.6(3), N3-Pt1-N4 64.6(4).

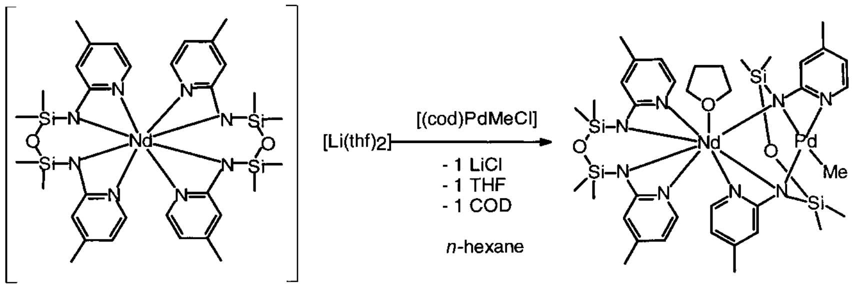
Mechanism of the ligand-transfer reaction: The ligand-transfer reaction probably proceeds via a heterobimetallic intermediate (**1a**) (Scheme 2). It is plausible to assume that after **1a** is generated, another heterobimetallic structure **1b** with a



Scheme 2. Proposed mechanism of the ligand-transfer reaction.

μ-chloro bridge between the neodymium atom and the platinum atom is generated. The final step in this mechanism is the transfer of the bisaminopyridinato ligand to the platinum atom, and the transfer of the chloro functionality to the neodymium atom. Compound **7** (see Scheme 3), a model for such an intermediate and the resulting products (**4** and **5**), provides evidence to support these mechanistic considerations.

The heterobimetallic complex **7** was formed as a light yellow powder from the reaction of **1** with [(cod)PdMeCl][14] in hexane (Scheme 3). Crystals of **7** suitable for an X-ray structure analysis (Table 1) were obtained from a mixture of hexane and THF (1:3). The molecular structure of the Nd-Pd-Me complex **7** (Figure 3) shows a planar coordination of the Pd atom, characteristic of Pd^{II} compounds. The Nd–Pd distance is 3.0345(12) Å. The two metal centers are bridged by one bis(Ap) ligand, whereas the other bis(Ap) ligand is coordinated at the neodymium center. Similar to the bonding situation of compound **4**, the Ap fragment in **7** is strained in its connection to Pd, as shown by a N-Pd-N angle of 64.9(3)°. The stability of **7** compared with that of the intermediate **1a** can be explained by the inhibited transfer of the methyl group to the lanthanide center. The methyl group is a weaker leaving group than the chloro functionality and does not have lone pairs to form the proposed bridged intermediate. Furthermore, the stability of lanthanide methyl compounds of the type $[O(SiMe_2Ap)_2LnMe(thf)_n]$ is expected to be lower than for the corresponding chloro complexes **5** and **6**.[15]



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Scheme 3. Synthesis of **7**.

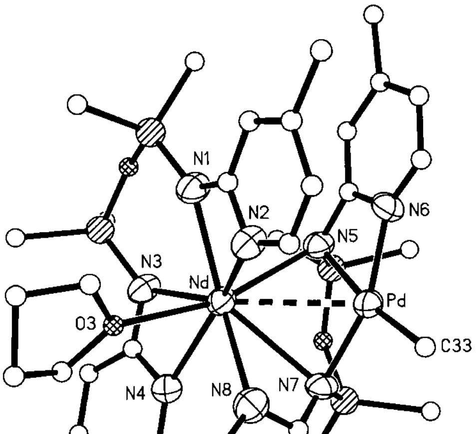
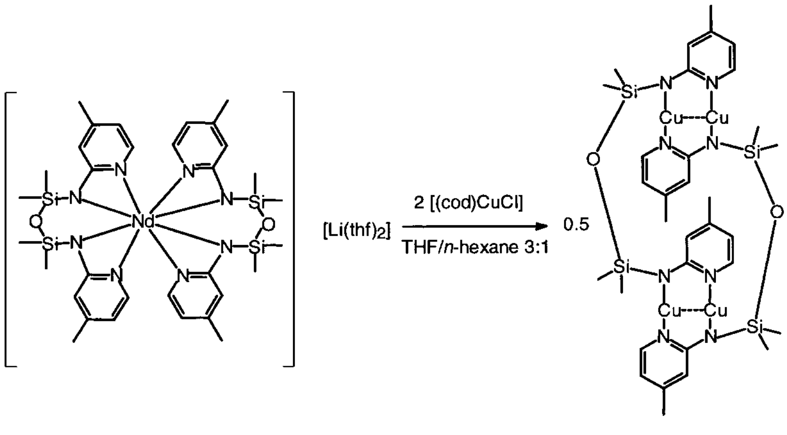


Figure 3. Molecular structure of **7** (ORTEP view; for clarity only atoms regarded significant are drawn as 30% propability ellipsoids). Selected bond lengths [Å] and angles [°]: Nd–-N3 2.475(8), Nd–N1 2.480(8), Nd–N2 2.542(9), Nd–N4 2.547(9), Nd–N8 2.612(9), Nd–N5 2.659(8), Nd–N7 2.761(8), Nd–Pd 3.0345(12), Pd–N6 2.048(9), Pd–N7 2.062(8), Pd–N5 2.187(8); N3-Nd-N1 84.8(3), N1-Nd-N2 54.4(3), N3-Nd-N4 54.0(3), C33-Pd-N6 104.7(4), C33-Pd-N7 95.3(4), N6-Pd-N5 64.9(3), N7—Pd-N5 95.1(3).

Ethylene oligomerization studies: Complex **3** was investigated with regard to catalytic applications in ethylene oligomerization after activation with alkylaluminum compounds. By using $EtAlCl_2$ (Al/Ni 150) in hexane at room temperature as an activator, oligoethylenes with mainly internal double bonds (Schulz–Flory distribution, TOF = 2400 h^{-1}) were observed. Highly branched oligomers with a very narrow molecular weight distribution ($M_n = 230\,g\,mol^{-1}$ (relative to polystyrene standards), $M_w/M_n = 1.14$) are formed when $Et_3Al_2Cl_3$ is employed as a cocatalyst and CH_2Cl_2 as the solvent (TOF = 122000 h^{-1}). The ethylene consumption is nearly constant in both experiments. The products of the second oligomerization experiment are identical, according to the results of NMR investigations, with results recently published by Sen et al.[16] A comparison of these two systems indicates that the activity of **3** is orders of magnitude higher.

Porous materials, synthesis and structure: If one equivalent of **1** or **2** is treated with two equivalents of [(cod)CuCl], a ligand-transfer reaction takes place (Scheme 4). The product of this conversion is a polycyclic, tetranuclear complex **8**, which shows interesting structural features. Crystals of **8** suitable for X-ray structure analysis (Table 1) were obtained from a mixture of THF/hexane (3:1) at −30 °C. The molecular structure is shown in Figure 4. This copper complex shows an almost linear coordination at the copper centers. The metal atoms are surrounded by one pyridine and one amido functionality. The $N_{pyridine}$-Cu-N_{amido} angles are 174.1(3)° and 177.3(3)°. With help of the metal and framework atoms of two aminopyridinato fragments, a fourteen-membered ring system is formed, in which the ring atoms are arranged in a nearly planar fashion. The short Cu–Cu distance is 2.4294(13). The Cu–Cu interatomic distances in aminopyridinato-bridged dimeric Cu^I complexes range from 2.42–2.60 Å.[7] The shortest Cu^I–Cu^I distance reported so far (to the best of our knowledge) is 2.348(2) Å.[6d] The Cu–N bond lengths in **8** are nearly the same, and the Ap systems can be assumed to have the same delocalized binding mode as found in similar systems.[7] The NMR investigation (CD_2Cl_2) shows, as expected for the highly symmetric molecule, a single-signal set. The solid-state structure of **8** is particularly interesting (Figure 5), because of the formation of channels due to the



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Scheme 4. Synthesis of **8**.

sequential ordering of the large fourteen-membered rings. Low- coordinate transition metals are placed in these channels. Intensive investigation of crystalline and porous systems based on coordination compounds as well as anionic ligands, and thus on covalent bonding instead of a connectivity resulting from simple donor interactions, is currently being carried out, since a lot of applications are expected from such systems.[17]

Remarks concerning the synthesis of the amido metal complexes by salt elimination reactions: The synthesis of **3**, **4**, and **8** does not work, irrespective of the solvent and/or temperature variations, when using the dilithiated ligand precursor [$O(SiMe_2Ap\text{-}Li)_2$] and [$(dme)NiCl_2$], [$(cod)PtCl_2$], or [(cod)CuCl]. A reduction of nickel and copper is observed. The use of amines, for example Et_3N, instead of BuLi as a deprotonating agent is also ineffective. Studies are continuing in the search for easier ways to synthesize these compounds; however, to date the method described appears the most successful.

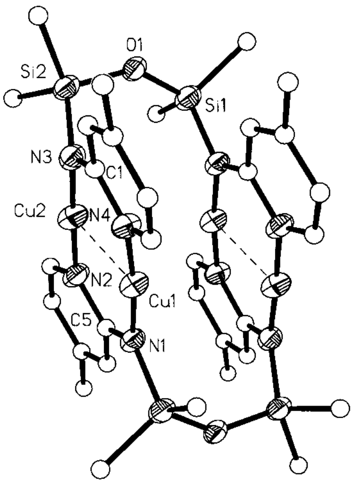

Figure 4. Molecular structure of **8** (ORTEP view; for clarity only atoms regarded significant are drawn as 30% propability ellipsoids). Selected bond lengths [Å] and angles [°]: N1–Cu1 1.866(5), N2–Cu2 1.878(6), N3–Cu2 1.884(6), N4–Cu1 1.879(6), Cu1–Cu2 2.4294(13); Si2-O1-Si1 139.4(3), N3-C1-N4 119.4(6), N2-C5-N1 119.0(6), N1-Cu1-N4 174.1(2), N1-Cu1-Cu2 89.6(2), N4-Cu1-Cu2 88.2(2), N2-Cu2-N3 177.3(3), N2-Cu2-Cu1 88.0(2), N3-Cu2-Cu1 89.3(2).

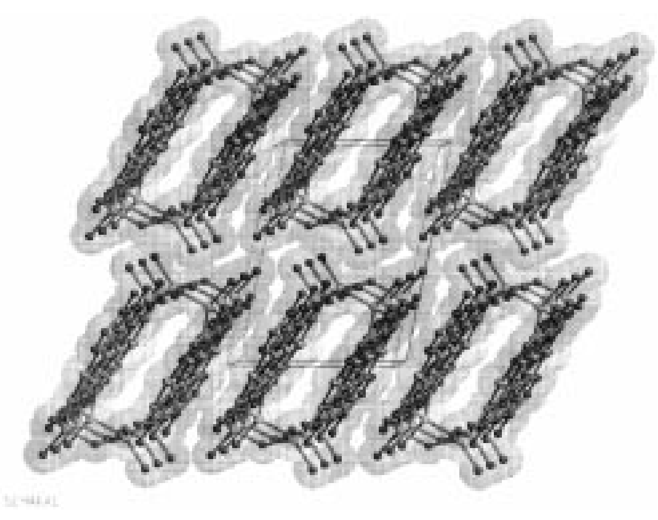

Figure 5. Solid-state structure of **8**.

Conclusion

The "ate" complex mediated ligand transfer (Scheme 1 and Scheme 4) can formally be considered as a specific modification of the reactivity of lithium amides at lanthanide centers. The amides are modified in their reactivity and reductive capability via coordination at the lanthanide center. They show a reactivity high enough to react with chloro compounds of electron-rich late transition metals but these metals are not reduced. Unstable Ln–Ni, Ln–Pt, or Ln–Cu heterobimetallic complexes can be assumed as intermediates of the lanthanide-mediated ligand-transfer reactions.[18a] These intermediates are most likely important for the formation of the polycyclic and multinuclear structures of the resulting late transition metal amido complexes such as **3** and **8**.

Experimental Section

General: The neodymium- (**1**) and lanthanum-"ate" (**2**) complexes were prepared according to a previously published procedure.[18] [(cod)PdMeCl] was prepared according to the literature.[14] All other reagents were obtained commercially (Strem) and used as supplied. All manipulations were performed with rigorous exclusion of oxygen and moisture in dried Schlenk-type glassware on a dual manifold Schlenk line, or in an argon-filled glovebox (mBraun labmaster 130) with a high-capacity recirculator (< 1.5 ppm O_2). Solvents (Aldrich, Fluka) and NMR solvents (Cambridge Isotop Laboratories, all 99 atom% D) were freshly distilled from sodium tetraethylaluminate. NMR spectra were recorded on a Bruker ARX 400 instrument at 297 K. ^1H and ^{13}C chemical shifts are referenced to the solvent resonances and reported relative to TMS. ^{29}Si chemical shifts are reported relative to TMS. The magnetic moment of **7** was measured by employing the method of Evans.[19] IR spectra were recorded on a Nicolet Magna 550 instrument (Nujol mulls using KBr plates). Melting points were determined in sealed capillaries on a Büchi 535 apparatus. Elemental analysis was performed with a Leco CHNS-932 elemental analyzer. X-ray diffraction data were collected on a Stoe-IPDS-diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. The crystals were mounted in a cold nitrogen stream or sealed inside a capillary. The structure was solved by direct methods (SHELXS-86)[20] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[21] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-125420 (**3**), CCDC-148808 (**4**), CCDC-100884 (**7**), and CCDC-125420 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Complex syntheses

Synthesis of [{O(SiMe$_2$-Ap)$_2$}$_2$Ni$_2$] (3): To a vigorously stirred suspension of **1** (985 mg, 1 mmol) in hexane (80 mL) was added solid [(dme)NiCl$_2$] (220 mg, 1 mmol). A dark blue color resulted within a few minutes. The suspension was stirred for 24 h at room temperature. The solution was filtered, and the volume was reduced under vacuum to approximately 30 mL. Cooling to −30 °C afforded a dark blue crystalline material. Yield: 411 mg (0.51 mmol, 51 %); m. p. >200 °C (decomp); ^{1}H NMR (400.13 MHz, C_6D_6): $\delta = 0.12$ (s, 6H), 0.33 (s, 6H), 0.58 (s, 6H), 1.33 (s, 6H) (Me−Si), 1.46 (s, 6H), 1.71 (s, 6H) (Me − Py), 5.46 (m, 2H, H5), 5.51 (m, 2H; H5), 5.67 (m, 2H; H3), 6.30 (d, $J = 5.5$ Hz, 2H; H6), 8.69 (d, $J = 6.0$ Hz, 2H; H6); ^{13}C NMR (100.62 MHz, C_6D_6): $\delta = -0.8$, −0.2, 0, 3.6 (Me−Si), 20.1, 18.8 (Me − Py), 107.9, 108.1 (C3), 111.2, 116.5 (C5), 140.2, 143.6 (C6), 145.9, 148.6 (C4), 169.5 171.0 (C2); ^{29}Si NMR (79.49 MHz, C_6D_6): $\delta = -9.5$, −13.2; IR (Nujol): $\tilde{\nu} = 1607$ vs, 1530 m (arom.), 1456 s br, 1417 s, 1325 s, 1299 s, 1283 m, 1250 s (Me−Si), 1216 m, 1178 s, 1125 w, 1039 m, 1009 vs (Si−O−Si), 974 m, 892 s, 851 m, 845 m, 798 vs (Me$_2$Si), 785 s, 746 m, 721 m, 679 w, 650 w, 614 m, 598 m, 563 w, 555 w, 453 m cm^{-1}; elemental analysis (%) for $C_{32}H_{48}N_8Ni_2O_2Si_4$ (806.51): calcd: C 47.66, H 6.00, N 13.89; found: C 47.83, H 5.95, N 13.66. The procedure described above also works when using **2** (999 mg, 0.95 mmol) and [(dme)NiCl$_2$] (209 mg, 0.95 mmol) with nearly the same yield.

Synthesis of [{O(SiMe$_2$-Ap)$_2$}Pt] (4): To a vigorously stirred suspension of **1** (887 mg, 0.9 mmol) in hexane (80 mL) was added solid [(cod)PtCl$_2$] (305 mg, 0.9 mmol). A yellow color resulted within a few minutes. The suspension was stirred for 24 h at room temperature. The solution was filtered, and the volume was reduced under vacuum to approximately 30 mL. Cooling to −30 °C afforded a yellow crystalline material. Yield: 136 mg (0.25 mmol, 28 %); m. p. >190 °C (decomp); ^{1}H NMR (400.13 MHz, C_6D_6): $\delta = 0.41$ (s, 6H) (Me−Si), 1.73 (s, 6H) (Me − Py), 5.41 (m, 1H; H5), 5.71 (m, 1H; H3), 5.41 (m, 1H; H5), 7.32 (d, $J = 5.55$ Hz, 1H; H6); ^{13}C NMR (100.62 MHz, C_6D_6): $\delta = 0.03$ (Me−Si), 20.4 (Me−Py), 109.1 (C3), 110.2 (C5), 143.8 (C6), 148.9 (C4), 176.6, 171.0 (C2); ^{29}Si NMR (79.49 MHz, C_6D_6): $\delta = -14.3$; IR (Nujol): $\tilde{\nu} = 1605$ vs, 1528 m (arom.), 1454 s br, 1376 s, 1289 s, 1283 m, 1247 s (Me−Si), 1178 s, 1120 w, 1037 m, 1004 vs (Si−O−Si), 975 m, 898 s, 853 m, 798 vs (Me$_2$Si), 786 s, 745 m, 721 m, 679 w, 650 w, 614 m, 598 m, 564 w, 562 w, 466 m, 449 m cm^{-1}; elemental analysis (%) for $C_{16}H_{24}N_4OPtSi_2$ (539.64): calcd: C 35.61, H 4.48, N 10.38; found: C 35.23, H 4.41, N 10.01. The procedure described above also works when using **2** (982 mg, 0.93 mmol) and [(cod)PtCl$_2$] (315 mg, 0.93 mmol) with nearly the same yield.

Synthesis of [{O(SiMe$_2$-Ap)$_2$}$_2$Nd(thf)PdMe] (7): Compound **1** (985 mg, 1 mmol) and [(cod)PdMeCl] (265 mg, 1 mmol) were suspended in hexane (60 mL) and stirred at room temperature for 16 h. The mixture was filtered, and the filtrate was concentrated under vacuum to approximately 15 mL. Cooling to −30 °C afforded a light yellow powder. Yield: 431 mg (0.42 mmol, 42 %), m. p. >280 °C. Crystals suitable for X-ray structural analysis were obtained from THF/hexane (1:4 v/v) solution; IR (Nujol): $\tilde{\nu} = 1604$ vs, 1546 m, 1531 w (arom.), 1328 m, 1291 m, 1250 s (Me − Si), 1177 m, 1026 s br (Si−O−Si), 970 m, 880 s, 847 m, 786 s (Me$_2$Si), 725 m, 581 w, 443 w cm^{-1}; $\mu_{eff} = 4.46\mu_B$; elemental analysis (%) for $C_{37}H_{59}N_8NdO_3PdSi_4$ (1026.93): calcd: C 43.28, H 5.79, N 10.91; found: C 43.05, H 5.88, N 10.72.

Synthesis of [{O(SiMe$_2$-Ap)$_2$}$_2$Cu$_4$] (8): To a solution of **1** (925 mg, 0.94 mmol) in THF/hexane (3:1 v/v; 80 mL) was added solid [(cod)CuCl] (331 mg, 1.6 mmol). The resulting suspension was stirred for 16 h at room temperature. After filtration the volume was reduced under vacuum to approximately 30 mL. Cooling to −30 °C afforded a light yellow crystalline material. Yield: 645 mg (0.68 mmol, 43 %); m. p. >259 °C (decomp); ^{1}H NMR (400.13 MHz, CD_2Cl_2): $\delta = 0.33$ (s, 24H) (Me−Si), 2.08 (s, 6H) (Me−Py), 5.67 (m, 4H; H3), 5.80 (d, $J = 5.6$ Hz, 4H; H5), 6.42 (s, 4H; H3), 7.12 (d, $J = 5.8$ Hz, 4H; H6); ^{13}C NMR (100.62 MHz, CD_2Cl_2): $\delta = 2.8$ (Me−Si), 21.3 (Me−Py), 111.3 (C3), 116.5 (C5), 147.3 (C6), 147.5 (C4), 167.7 (C2); ^{29}Si NMR (79.49 MHz, CD_2Cl_2): $\delta = -15.0$; IR (Nujol): $\tilde{\nu} = 1620$ vs, 1527 s (arom.), 1485 s, 1454 s br, 1377 m, 1329 s, 1287 m, 1249 s (Me−Si), 1189 m, 1117 w, 1032 m, 999 vs (Si−O−Si), 977 m, 900 s, 854 m, 813 m, 795 vs (Me$_2$Si), 774 m, 741 m, 727 m, 690 m, 677 w, 650 w, 643 w, 599 w, 574 w, 447 m cm^{-1}; elemental analysis (%) for $C_{32}H_{48}Cu_4N_8O_2Si_4$ (943.32): calcd: C 40.74, H 5.13, N 11.88; found: C 40.53, H 5.10, N 11.83.

Ethylene oligomerization studies: Oligomerization of ethylene (99.95 %) was carried out in a batch process using a 1-L-glass autoclave fitted with a gas inlet, dosing device, pressure gauge, and a magnetically driven and continuously regulated paddle stirrer with a hollow shaft (0–800 rpm). The solvents (hexane, dichloromethane) were dried by standard methods and rectified under argon. $EtAlCl_2$ and $Et_3Al_2Cl_3$ were commercial products (Aldrich).

The Ni complex (0.1 mmol), dispersed in 150 mL solvent, was introduced under inert conditions into the autoclave. After the temperature of the mixture was adjusted to 5 °C and the organoaluminum compound (1.5 mmol) was added as a cocatalyst, the oligomerization reaction was initiated at an internal pressure of 3.3 bar. After 7 h, the content of the autoclave was decomposed by methanolic HCl. With hexane as solvent, oligomers (4.7 g) were isolated (C_4–C_{24} alkenes and alkanes with a maximum at C_8; degree of saturation 60 %, percentage of linear olefins about 40 %). The activity was 2400 $\text{mol}_{\text{oligomers}}\,\text{mol}_{\text{Ni}}^{-1}\,\text{h}^{-1}$.

Under the same conditions, the oligomerization in dichloromethane yielded oligomers (22.8 g) after 40 min. In spite of intense cooling (−20 °C) the temperature rose to 45 °C. The activity was 122 000 $\text{mol}_{\text{oligomers}}\,\text{mol}_{\text{Ni}}^{-1}\,\text{h}^{-1}$. The oligomers with a maximum at $>C_{24}$ were highly branched: ratio of methyl protons (at $\delta = 0.87$)/total alkyl protons (by ^{1}H NMR integration) equals 0.61. An important amount of the oligomeric product was saturated (85 % by GC-IR).

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[1] M. F. Lappert, P. P. Power, A. R. Sanger, R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Norwood Ltd., Chichester, England, **1980**.

[2] a) R. Kempe, *Angew. Chem.* **2000**, *112*, 478–504; *Angew. Chem. Int. Ed.* **2000**, *39*, 468–493; b) M. D. Fryzuk, T. S. Haddad, D. J. Berg, S. J. Rettig, *Pure Appl. Chem.* **1991**, *63*, 845–850; c) M. D. Fryzuk, *Can. J. Chem.* **1992**, *70*, 2839–2845; d) F. T. Edelmann, *Coord. Chem. Rev.* **1994**, *137*, 403–481; e) H. Brand, J. Arnold, *Coord. Chem. Rev.* **1995**, *140*, 137–168; f) C. Floriani, *Chem. Commun.* **1996**, 1257–1263; g) C. Floriani, *Pure Appl. Chem.* **1996**, *68*, 1–8; h) J. G. Verkade, *Acc. Chem. Res.* **1993**, *26*, 483–489; i) R. R. Schrock, *Acc. Chem. Res.* **1997**, *30*, 9–16; j) R. R. Schrock, *Pure Appl. Chem.* **1997**, *69*, 2197–2203; k) C. C. Cummins, *Chem. Commun.* **1998**, 1777–1786; l) C. C. Cummins, *Prog. Inorg. Chem.* **1998**, *47*, 685–836; m) J. Barker, M. Killner, *Coord. Chem. Rev.* **1994**, *133*, 219–300.

[3] M. D. Fryzuk, C. D. Montgomery, *Coord. Chem. Rev.* **1989**, *95*, 1–40.

[4] a) R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539; b) R. G. Pearson, *J. Chem. Educ.* **1968**, *45*, 581–586; c) R. G. Pearson, *J. Chem. Educ.* **1968**, *45*, 643–65.

[5] Examples of amidonickel complexes: a) D. C. Bradley, M. B. Hursthouse, R. J. Smallwood, A. J. Welch, *J. Chem. Soc. Chem. Commun.* **1972**, 872–873; b) M. D. Fryzuk, P. A. MacNeil, *J. Am. Chem. Soc.* **1981**, *103*, 3592–3593; c) M. D. Fryzuk, P. A. MacNeil, S. J. Rettig, A. S. Secco, J. Trotter, *Organometallics* **1982**, *1*, 918–930; d) H. Hope, M. M. Olmstead, B. D. Murry, *J. Am. Chem. Soc.* **1985**, *107*, 712–713; e) R. A. Barlett, H. Cheng, P. P. Power, *Angew. Chem.* **1989**, *101*, 325–327; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 316–318; f) P. T. Matsunaga, C. R. Hess, G. L. Hillhouse, *J. Am. Chem. Soc.* **1994**, *116*, 3665–3666; g) K. Koo, G. L. Hillhouse, *Organometallics* **1995**, *14*, 4421–4423; h) D. D. VanderLende, K. A. Abboud, J. M. Boncella, *Inorg. Chem.* **1995**, *34*, 5319–5376; h) P. L. Holland, R. A. Andersen, R. G. Bergman, *J. Am. Chem. Soc.* **1996**, *118*, 1092–1104; b) P. L. Holland, R. A. Andersen, R. G. Bergman, J. Huang, S. P. Nolan, *J. Am. Chem. Soc.* **1997**, *119*, 12800–12814.

[6] Examples of amidocopper complexes: a) L.-P. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B. Hathaway, C. Simmons, P. Thornton, *J. Chem. Soc. Dalton Trans.* **1990**, 3835–3840; b) K. Dehnicke, *Chem. Ztg.* **1990**, *114*, 295–304; c) S. Maier, W. Hiller, J. Strähle, C. Ergezinger, K. Dehnicke, *Z. Naturforsch.* **1988**, *43 b*, 1628–1632; d) J. Beck, J. Strähle, *Angew. Chem.* **1985**, *97*, 325–327; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 409–410.

[7] Examples of amidocopper complexes related to **8**: a) L. M. Engelhardt, G. E. Jacobsen, W. C. Patalinghug, B. W. Skelton, C. L. Raston, Allan H. Withe, *J. Chem. Soc Dalton Trans* **1991**, 2859–2868; b) S. W. Lee, W. C. Trogler, *Inorg. Chem.* **1990**, *29*, 1659–1662; c) H. Aghabozorg, S. Gambarotta, C. Bensimon, *J. Sci. I. R. Iran* **1994**, *5*, 158–162.

[8] C. Mechtler, R. Kempe, Ch. Marschner, *Organometallics*, submitted.

[9] a) M. Oberthür, P. Arndt, R. Kempe, *Chem. Ber.* **1996**, *129*, 1087–1091; b) A. Spannenberg, P. Arndt, M. Oberthür, R. Kempe, *Z. Anorg. Allg. Chem.* **1997**, *623*, 389–393; d) M. Oberthür, G. Hillebrand, P. Arndt, R. Kempe, *Chem. Ber./Recueil* **1997**, *130*, 789–794; e) R. Kempe, M. Oberthür, G. Hillebrandt, A. Spannenberg, H. Fuhrmann, *Polimery* **1998**, *43*, 96–103.

[10] A. Spannenberg, P. Arndt, R. Kempe, *Angew. Chem.* **1998**, *110*, 824–827; *Angew. Chem. Int. Ed.* **1998**, 37, 832–835.

[11] J. Campora, J. A. Lopez, P. Palma, C. Ruiz, E. Carmona, *Organometallics* **1997**, *16*, 2709–2718.

[12] N. N. Greenwood, A. Earnshaw, *Chemie der Elemente*, VCH, Weinheim, **1988**, p. 1479.

[13] D. R. Lide, CRC Handbook of Chemistry and Physics, CRC Press, Boston, **1990**.

[14] R. E. Rülke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen, K. Vriez, *Inorg. Chem.* **1993**, *32*, 5769–5778.

[15] F. T. Edelmann, *Angew. Chem.* **1995**, *107*, 2647–2669; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2466–2488.

[16] J. S. Kim, J. H. Pawlow, L. M. Wojcinski II, S. Murtuza, S. Kacker, A. Sen, *J. Am. Chem. Soc.* **1998**, *120*, 1932–1933.

[17] a) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276–279; b) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, Science **1999**, *283*, 1148–1150.

[18] a) A. Spannenberg, M. Oberthür, H. Noss, A. Tillack, P. Arndt, R. Kempe, *Angew. Chem.* **1998**, *110*, 2190–2192; *Angew. Chem. Int. Ed.* **1998**, *37*, 2079—2082; b) H. Noss, M. Oberthür, C. Fischer, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **1999**, 2283–2288.

[19] a) D. F. Evans, *J. Chem. Soc.* **1959**, 2003–2005; b) J. L. Deutsch, S. M. Poling, *J. Chem. Educ.* **1969**, *46*, 167–168; c) J. Löbiger, R. Scheffold, *J. Chem. Educ.* **1972**, *49*, 646–647.

[20] G. M. Sheldrick, *Acta. Crystallogr. Sect. A* **1990**, *46*, 467.

[21] G. M. Sheldrick, University of Göttingen, **1993**.

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